Low Cost and Reliable Sodium-Metal Halide(Na-MH) Batteries for Stationary Energy Storage Application

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ABSTRACT

Stationary electric energy storage devices have gained increasing prominence due to great market needs such as improving the sustainability of renewable energy resources and supporting the reliability of the electric grid. Among various battery technologies, with regard to raw materials availability, sodium based batteries are better positioned than lithium batteries due to the abundance of sodium in the earth's crust. However, the sodium-metal halide (Na-MH) battery, one of the most attractive stationary battery technologies, is hindered from further market penetration by an expdited material degradation and high manufacturing cost at high operating temperatures. This work focuses on developing advanced Na-MH battery technologies by lowering the operating temperature below 200°C for a longer cycle life. In particular, lowering the operating temperature of a Na-MH battery opens great opportunities to adopt cost-effective sealing technologies (polymer seals) for the cell architecture to replace high cost sealing methods.

Keywords: Na-metal halide battery, Ni, stationary energy storage, β "-alumina, polymer sealing

1. INTRODUCTION

Electrochemical energy storage devices (rechargeable batteries) have gained increasing attention for transportation and grid-scale applications [1-3]. In particular, Na-metal halide (Na-MH) batteries are considered as one of the most important battery technologies for next-generation stationary energy storage systems due to highly abundant and low cost Na resources and suitable reduction potential (-2.7 V vs. a standard hydrogen electrode) [4, 5]. Sodium-nickel chloride (Na-NiCl₂) is the most extensively investigated redox couple among various Na-MH battery redox chemistries reported in the literature [6-9]. The overall redox reaction of a Na-NiCl₂ battery during charge and discharge processes is as follows [10]:

(Discharged state) $2NaCl + Ni \leftrightarrow 2Na + NiCl_2$ (Charged state), $E_0 = 2.58$ V at $300^{\circ}C$.

The essential parts of Na-NiCl₂ systems are a molten sodium anode, a β'' -alumina solid-state electrolyte (BASE), a secondary electrolyte, and a metal-halide cathode [10, 11]. A Na-NiCl₂ battery can be assembled in a fully discharged state, using sodium chloride (NaCl) and Ni powders without handling extremely pyrophoric metallic sodium and hygroscopic metal halides [12]. The BASE, a sodium-ion conducting ceramic, prevents crossover and battery selfdischarge (100% coulombic efficiency) for a broad range of operational conditions. Furthermore, the use of an inorganic secondary electrolyte, sodium aluminum tetrachloride (NaAlCl₄), provides high Na⁺ ion conductivity and superior battery safety [13].

Typically, a conventional tubular type Na-NiCl₂ battery is operated at high temperatures above 280°C to obtain acceptable electrochemical performance [14]. To mitigate the materials corrosion and degradation at such high temperatures, complicated and high cost sealing technologies including glass sealing between BASE tubes and α -Al₂O₃ rings, thermal compression bonding (TCB) between metallized α -Al₂O₃ rings and metal blocks, and electron beam welding between metal blocks and cell cases, are essential for the tubular cell to achieve a hermetic seal [14, 15]. Despite their attractive features, tubular type Na-MH batteries have not achieved further market penetration because of challenges including complicated cell architecture, high cell manufacturing cost, high operating temperature, and degradation of battery performance with cycling.

On the other hand, planar cell designs can offer overwhelming advantages in terms of power output, cell packaging, ease of assembly, and thermal management [16]. Moreover, our recent work on a planar type Na-NiCl₂ battery demonstrated that remarkable electrochemical performance can be achieved even at an intermediate temperature of 190°C [17]. The overall electrochemical performance of Na-NiCl₂ batteries at 190°C exhibits a stable cycle life of over 1000 cycles with an excellent capacity retention. The high energy density and superior cycle stability are attributed to the slower particle growth of cathode materials (NaCl and Ni) at 190°C compared to that at 280°C [17]. Unfortunately, constructing planar type Na-MH batteries with a large active area has not been highly successful in the past. The main reason is that performing TCB seals on a large area is extremely difficult due to the large thermal mismatch during the TCB process. Lowering the operating temperature of a Na-NiCl₂ battery from 280°C to 190°C opens great opportunities, not only to adopt cost-effective sealing technologies, but also to mitigate the challenge of designing large planar type Na-MH batteries through replacing TCB with compliant polymer seals.

Here we present a compliant sealing technology using conventional polymer materials for planar type Na-NiCl₂ batteries. Polymers chosen for thermal and chemical stability are implemented in Na-NiCl₂ cells. The compatibility of polymer seals is investigated by monitoring the electrochemical performance during cell cycling. The polymer-sealed cells could be cycled more than 700 times with stable cell performances. Use of the conventional polymers demonstrated in this work can be a cost-effective, reliable, and practical solution for Na-MH battery technologies, and provides a great opportunity for developing low cost planar sodium battery technologies.

2. EXPREIMENTAL

2.1 BASE Fabrication



Figure 1 Schematic view of BASE fabrication process

BASE discs used in this work were fabricated by converting α-Al₂O₃ discs through a vapor phase process shown in Fig. 1. Briefly, 70 vol%, high purity α -Al₂O₃ (Almatis A16-SG, >99.8%) and 30 vol% YSZ (Imerys Fused Minerals Murg GmbH, 8 wt% yttria-stabilized zirconia, 2 µm, high purity) were mixed by high energy attrition milling in isopropanol to achieve a median particle size (d_{50}) less than 0.5 µm (step #1). Then the powders were continuously mixed with methyl ethyl ketone/ethanol (4:1), dispersant (PS-131), a binder (polyvinyl butyral), and a plasticizer (benzyl butyl phthalate) using lowenergy ball milling to make slurry (step #2). In step #3, the slurry was cast into thin sheets (\sim 125 µm) using a tape caster, and the sheets were laminated and laser cut into 3 cm diameter discs. Then the discs were fired at 1500°C in air to obtain fully sintered α -Al₂O₃/YSZ discs (step #4). Finally (step #5), the sintered α -Al₂O₃/YSZ discs were buried in loose β "-Al₂O₃ powder and heat treated at 1450°C in air to convert α-Al₂O₃ into β "-Al₂O₃. The conversion occurs by simultaneous transport of sodium cations and oxygen anions from the β "-Al₂O₃ powders to the α -Al₂O₃/YSZ discs. The thickness of the converted composite β "-Al₂O₃/YSZ discs is 500–600 µm.

2.2 Cathode and Melts Preparation

Cathode materials in the discharged state consist of 62.2 wt% Ni (Novamet, Type 255), 34.2 wt% NaCl (Alfa Aesar, 99.99%), and 3.6 wt% additives (FeS, aluminum powder, NaI, and NaF, Sigma Aldrich). The cathode powders were thoroughly mixed using a low-energy ball milling method in a nitrogen environment. Then, well-mixed cathode powders were turned into granules using a granulator (Freund TF-Labo) chamber with flowing nitrogen. Sodium in а tetrachloroaluminate (NaAlCl₄), the melt, was prepared by a high temperature reaction (up to 320°C) using NaCl and AlCl₃ powders in an inert environment.

2.3 Cell Tesings and Polymer Screening

As shown in Fig. 2, a planar type cell configuration consists of cell end caps (stainless steel), α -alumina (99.5% purity) fixture, cathode materials, anode shim, and polymer washers. First, a BASE disc was glass-sealed to an α -alumina fixture, and the anode side of the BASE disc was pretreated with an aqueous lead acetate (Pb[CH₃COO]₂) solution followed by a heat treatment at 400°C. The fixture was then transferred into a nitrogen-purged glove box for the cell assembly. 1 g of cathode granules was added to the cathode side of the fixture and 0.7 g of melt was vacuum infiltrated into the granules at an elevated temperature of 200°C. Finally, the fixture was enclosed with end caps by compression sealing using polymer washers. Initially, all cells were cycled at 190°C between the cutoff voltages of 2.8 V (charge limit) and 1.8 V (discharge limit) at a constant current of 10 mA for conditioning cycles. After the initial conditioning cycles, fixed-capacity cycling tests were conducted at a charge current of 20 mA (C/4.5) and a discharge current of 30 mA (C/3). The capacity window for the cycling tests was between 22% (35 mAh) and 80% (125 mAh) of the state of charge (SOC) window (90 mAh, 58% of theoretical capacity). All cell tests were conducted using an Arbin potentiostat (MSTAT 8000). Prescreening tests for polymers were performed in a glove box on eight different types of polymer films: ultra-high-molecular-weight polyethylene polyvinylidene fluoride (UHMW-PE), (PVDF). polytetrafluoroethylene fluorinated ethylene (PTFE), propylene (FEP), perfluoroalkoxy alkane (PFA), polyether ether ketone (PEEK), polyimide (Kapton), and ultratemperature polyetherimide (Ultem PEI), purchased from McMaster-Carr. Na and NaAlCl4 (secondary electrolyte) in glass vials were placed on a 200°C hot plate and the polymers were soaked in the molten Na and NaAlCl4 for an extended period of time (>72 h).





3. RESULTS AND DISCUSSION

3.1 Prescreening of Polymers

Prescreening tests were conducted to evaluate the stability of polymers toward NaAlCl₄ and Na. Along with the primary purpose of using polymers as a sealing method, when selecting materials for the battery operation it is important to consider possible polymer decomposition from secondary electrolytes such as NaAlCl₄ in cathodes and from molten sodium anodes, as well as their melting temperatures. Four (PTFE, FEP, PFA, and UHMW-PE) out of the eight high temperature polymers were nonreactive with NaAlCl₄ melt, suggesting suitable sealing candidates for cathodes, while only two of them (PVDF, UHMW-PE) were stable with molten sodium anodes at 200°C. The rest of the polymers underwent color changes indicating chemical reactions with Na or NaAlCl₄.

3.2 Anode Seals



Figure 3 EOC and EOD voltage plots of cells with PVDF and UHMW-PE on the anode, respectively.

PVDF and UHMW-PE were applied to the anode sides of the cell fixtures (with FEP at the cathodes) to evaluate their thermal and chemical stability during cycling. The assembled cells were cycled in a fixed-capacity window between 22% and 80% SOC to demonstrate their compatibility with the Na-NiCl₂ system operating at 190°C; the performance of the cells is shown in Fig. 3. Voltages at the end of charge (EOC) and the end of discharge (EOD), at around 2.7 V and 2.3 V, respectively, were fairly stable throughout the cycles for the cell using PVDF as anode seal, suggesting that the cell has been effectively protected from air leakage. A gradual increase in EOD voltage (improvement of the cell performance) was observed, and it is attributed to improvement of wettability of molten Na on the BASE as well as effective protection of the anode from air by the use of the polymer sealing technique. The cell with UHMW-PE also shows no significant degradation over 100 cycles. However, continuous fluctuation with a slight decrease in EOD was observed, indicating a gradual discharge capacity problem on the anode side. Generally, PVDF (-(CF2-CH2)n-) and UHMW-PE (-(CH2-CH₂)_n-) have a similar backbone except half the -CH₂ is replaced by -CF₂ in PVDF. Because of the shielding effect of the F atoms in CF₂ adjacent to CH₂ groups, PVDF typically has higher melting temperature and mechanical strength than UHMW-PE. Also, PVDF is highly resistant to most inorganic/organic acids, bases, hydrocarbons, and oxidizing agents. We assume that these aspects could play a significant role when PVDF is used as sealing material between the cell fixture and the cell end cap for effectively protecting the anode from air without any side reactions with molten Na.

3.3 Cathode Seals

Since FEP, PFA, and PTFE are chemically stable with secondary electrolyte in the cathode at 190°C, these polymers were applied to the cathode side as sealing materials. The

anode side of the cells was sealed with a PVDF film, since its suitability on the anode side had been verified. A cell using a gold metal O-ring on the cathode side (with PVDF on the anode side) was tested as a reference cell since gold has strong chemical inertness toward cathode materials and good durability in air at high temperatures. Fig. 4 shows the voltages at EOC for the cells using gold, FEP, PFA, and PTFE. In order to obtain the degradation rate of each cell, a linear fitting analysis of the EOC voltages over 100 cycles was conducted. As expected, the reference cell shows very stable EOC voltage at around 2.7 V over 100 cycles. The cell with FEP also provides excellent EOC voltage stability, which suggests good compatibility as cathode-side sealing. In contrast to the cells using gold and FEP, the other two cells, with PFA and PTFE, show slightly more increase in the EOC voltage. This implies that oxidation of the Ni cathode during charging has been limited by the evaporation of melts or cathode degradation. Although all three fluorinated polymers have very similar chemical and general properties, such as melting point, thermal expansion, and thermal conductivity, FEP has remarkably lower absorption of water compared to PFA and PTFE. This suggests that FEP could be the most effective material for preventing cathode degradation and melt evaporation.



Figure 4 EOC voltage plots of cells with four different cathode seals.

3.4 Long-term Cycling

Indeed, Na-NiCl₂ cells assembled with FEP/PVDF (cathode/anode) present remarkable cell cycling stability over 700 cycles (Fig. 5). Voltage profiles of cells at 1st, 400th, and 700th cycle show very similar trends (Fig. 5a) except for EOC and EOD, in which a small voltage degradation was observed. To obtain more quantitative analysis on the cell degradation rate, area-specific resistance (ASR) was calculated (Fig. 5b). The degradation of a Na-NiCl₂ battery having FEP/PVDF seals can be extrapolated by making a linear fit for the plot of ASR at EOC and EOD. As shown in Fig. 5b, the corresponding fade rates of EOC and EOD would be 0.017% and 0.028% per cycle, respectively. These fade rates are commensurate with cycle lives of 5500 and 3700 before the voltages of EOC and EOD reach 2.8 V (charge limit) and 1.8 V (discharge limit), respectively.



Figure 5 (a) Voltage profiles (cycles 1, 400 and 700) for cells sealed with FEP/PVDF. (b) ASR plots at EOC and EOD over 700 cycles.

4. CONCLUSIONS

Design of planar Na-MH batteries has been challenging for large-scale cell designs despite its tremendous advantages over the tubular configuration. In this work, we demonstrate the successful implementation of selected polymers as sealants at the intermediate temperature of 190°C. Effective prevention of air leakage is successfully achieved in whole cells using various polymers for at least 100 cycles, and the cell sealed with a combination of PVDF/FEP achieved the most stable battery performance (>700 cycles). Our study provides an effective, economical, and feasible solution to for designing the planar type Na-MH battery for practical applications.

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